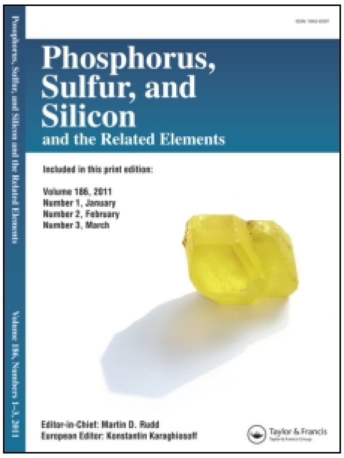

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PREPARATION AND STRUCTURE OF METAL COMPLEXES WITH THE LIGAND 2,4,6,8-TETRAMETHYL-2,4,6,8-TETRAAZA-1Λ^3-5Λ^3-DIPHOSPHABICYCLO [3.3.0]OCTAN-3,7-DIONE

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PREPARATION AND STRUCTURE OF METAL COMPLEXES WITH THE LIGAND 2,4,6,8-TETRAMETHYL-2,4,6,8-TETRAAZA-1λ^3-5λ^3-DIPHOSPHABICYCLO [3.3.0]OCTAN-3,7-DIONE*

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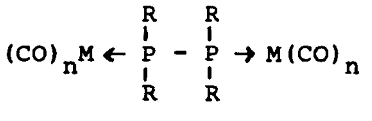
The reaction of the title compound with the metal carbonyls $Cr(CO)_5THF$, $Cr(CO)_4C_7H_8$, $Mo(CO)_4C_7H_8$ and $[Rh(CO)_2Cl]_2$ resulted in the formation of the metal complexes $P_2[meNC(O)NmeCr(CO)_5]_2$ **7**, $P_4[meNC(O)Nme]_4\,[Cr(CO)_4]_2$ **10**, $P_4[meNC(O)Nme]_4\,[Mo(CO)_4]_2$ **11** and $P_4[meNC(O)Nme]_4\,[Rh(CO)Cl]_2$ **12**. Under the reaction condition described no oxidative cleavage of the phosphorus-phosphorus-bond was observed. **10**, **11**, and **12** form six-membered rings containing four phosphorus and two metal atoms. The Lewis acids $SnCl_4$ and $SbCl_5$ react with the bicyclic biphosphine under formation of 1:1 $P_2[meNC(O)Nme]_2SnCl_4$ **8** and 2:1 $P_2[meNC(O)Nme]_2(SbCl_5)_2$ **9** adducts. The structures of chromium-pentacarbonyl complex $P_2[meNC(O)Nme]_2Cr(CO)_5$ **6** and bis(chromiumtetracarbonyl)-bis(μ-2,4,6,8-tetramethyl-2,4,6,8-tetraaza-1λ^4-5λ^4-diphospha-bicyclo[3.3.0]octan-3,7-dione] **10** has been determined by single-crystal X-ray diffraction. **6** crystallizes in the monoclinic space group $P2_1/c$ with unit cell constants $a = 13.003(3)$, $b = 9.924(2)$, $c = 14.577(3)$ Å, $\beta = 109.83(1)°$ and $Z = 4$. Full-matrix least-squares refinement of the structure converged with $R = 0.078$ and $R = 0.066$ for 1615 reflections with $I > 2.0\sigma(I)$. **10** crystallizes in the orthorhombic space group *Pnma* with unit cell constants $a = 11.270(1)$, $b = 19.497(3)$, $c = 14.389(4)$ Å and $Z = 4$. Full-matrix least-squares refinement yielded the terminal values $R = 0.108$ and $R = 0.091$ for 717 reflections with $I > 2.0\sigma(I)$. The λ^3P-λ^4P and λ^4P-λ^4P distances in **6** and **10** respectively are similar [2.217(4) and 2.22(1) Å].

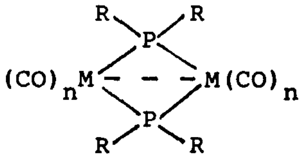
INTRODUCTION

The reaction of diphosphines with metal carbonyls have been investigated[1] and lead typically to complexes of type **1** and **2**. In **2** the phosphorus–phosphorus bond is cleaved and a metal–metal bond formed. More recently, it has been shown that the pyrolysis of **1** leads to the six membered rings **3** and other by-products.[2]



$$(CO)_nM \leftarrow \underset{R}{\overset{R}{P}} - \underset{R}{\overset{R}{P}} \rightarrow M(CO)_n$$

1



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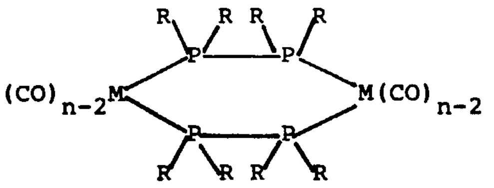
* Dr. Herbert Bestian in Dankbarkeit zum 70. Geburtstag gewidmet.



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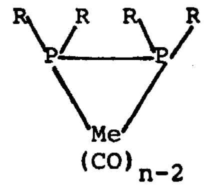

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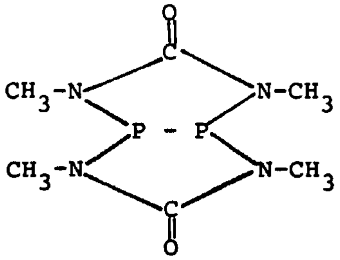


5

To our knowledge compounds of type **4** are not known. From several reactions we have found out that in the title compound **5** the phosphorus–phosphorus bond is stable towards oxidative cleavage.^{3} We decided to investigate the reaction of **5** with various metal carbonyls and Lewis acids in an attempt to prepare selectively compounds of type **1**, **3**, and **4**.

EXPERIMENTAL SECTION

The ^{1}H- and ^{31}P-n.m.r. spectra were recorded on a Bruker 60E and HX 90. $Si(CH_3)_4$ and 85% H_3PO_4, respectively, were used as external standards. Mass spectra were measured with a Varian MATCH 5 and i.r. spectra on a Perkin Elmer 735B. $P_2[meNC(O)Nme]_2^3$ **5** and $P_2[meNC(O)Nme]_2 \cdot Cr(CO)_5^3$ **6** were prepared according to previously reported procedures.^{3}

Bis(chromiumpentacarbonyl)-bis(μ-2,4,6,8-tetramethyl-2,4,6,8-tetraaza-1λ^4-5λ^4-diphospha-bicyclo[3.3.0]-octan-3,7-dione) 7. A solution of 2.14 g (8.1 mmol) $Cr(CO)_5THF$ in 240 ml THF was added dropwise to a solution of 0.95 g (4 mmol) **5** in 30 ml THF. After 3 days of stirring the solvent was removed. Recrystallization from THF resulted in colorless crystals of **7** in 72% yield (1.8 g). Anal. calcd. for $C_{16}H_{12}Cr_2N_4O_{12}P_2$: C, 31.08; H, 1.96; Cr, 16.8; N, 9.06; P, 10.02. Found: C, 30.9; H, 2.1; Cr, 16.5; N, 8.9; P, 9.9. IR data (Nujol): 2070 m, 2000 sh, 1990 sh, 1970 sh, 1940 s, 1700 s, 1425 w, 1410 w, 1320 m, 1260 m, 1220 w, 1180 w, 1095 w, 1020 w, 980 w, 950 m, 900 w, 850 w, 820 w, 650 sh, 640 cm^{-1} s. The mass spectrum exhibited a molecular ion (m/e 618, 8% relative intensity) and peaks corresponding to M-$(CO)_5$ (506, 18%); $P_2(NCH_3CONCH_3)_2Cr$ (286, 98%); $P_2(NCH_3CONCH_3)_2$ (234, 69%); $P_2(NCH_3)_2CO$ (177, 53%); $PNCH_3$ (60, 100%).

Adduct of $SnCl_4$ and 2,4,6,8-Tetramethyl-2,4,6,8-tetraaza-1λ^3-5λ^3-diphospha-bicyclo[3.3.0]octan-3,7-dione 8. A solution of 0.7 g (2.68 mmol) $SnCl_4$ in 10 ml CH_2Cl_2 was added slowly to 0.6 g (2.69 mmol) **5** in 15 ml CH_2Cl_2. Immediately a white solid precipitated. Stirring for 3 h, filtration and washing with CH_2Cl_2 yielded 0.9 g (70%) **8**. Anal. calcd. for $C_6H_{12}Cl_4N_4O_2P_2Sn$: C, 14.57; H, 2.43; Cl, 28.68; N, 11.32; P, 12.53. Found: C, 14.5; H, 2.6; Cl, 28.4; N, 11.3; P, 12.6. IR data (Nujol): 1560 m, 1525 s, 1515 s, 1410 m, 1195 w, 1020 w, 980 s, 805 w, 765 m, 755 w, 720 w, 590 sh, 575 s, 555 s, 480 w, 410 w, 320 cm^{-1} s.

Adduct of $SbCl_5$ and 2,4,6,8-Tetramethyl-2,4,6,8-tetraaza-1λ^4-5λ^4-diphospha-bicyclo[3.3.0]octan-3,7-dione 9. A solution of 1.1 g (3.4 mmol) $SbCl_5$ in 15 ml CH_2Cl_2 was added to a stirred solution of 0.4 g (1.7 mmol) **5** in 10 ml CH_2Cl_2. A white precipitate is formed. After 3 h of stirring the product was filtered off. After washing with 5 ml of CH_2Cl_2 a 92% (1.3 g) yield of **9** was obtained. Anal. calcd. for $C_6H_{12}Cl_{10}N_4O_2P_2Sb_2$: C, 8.66; H, 1.44; N, 6.73; P, 7.44. Found: C, 9.0; H, 1.6; N, 6.8; P, 7.5. IR data

(Nujol): 1715 s, 1440 w, 1425 w, 1375 w, 1310 s, 1280 w, 1240 w, 1220 w, 1170 w, 975 s, 915 w, 840 m, 740 m, 680 m, 650 w, 620 w, 560 w, 530 m, 500 w, 400 w, 370 m, 350 m, 340 cm^{-1} w.

Bis(chromiumtetracarbonyl)-bis(μ-2,4,6,8-tetramethyl-2,4,6,8-tetraaza-1λ^4-5λ^4-diphospha-bicyclo[3.3.0] octan-3,7-dione) 10. 0.5 g (2.1 mmol) **5** and 0.54 g (2.1 mmol) $Cr(CO)_4C_7H_8$ in 40 ml toluene were refluxed for 15 min under a stream of dry nitrogen. After keeping the reaction mixture at 85°C for 4 h the solvent was removed. Recrystallization of the residue from CH_2Cl_2 gave 0.35 g (43%) yield of **10**. Anal. calcd. for $C_{20}H_{24}Cr_2N_8O_{12}P_4$:C, 30.13; H, 3.01; N, 14.06; P, 15.55. Found: C, 30.7; H, 3.5; N, 13.6; P, 15.4. IR data (Nujol): 2020 s, 1955 s, 1935 s, 1900 s, 1700 sh, 1680 s, 1425 w, 1410 w, 1360 w, 1310 s, 1215 w, 1170 w, 950 m, 820 m, 760 w, 640 s, 625 cm^{-1} sh.

Bis(molybdenumtetracarbonyl)-bis(μ-2,4,6,8-tetramethyl-2,4,6,8-tetraaza-1λ^4-5λ^4-diphospha-bicyclo[3.3.0] octan-3,7-dione) 11. A suspension of 1.1 g (4.7 mmol) **5** and 1.4 g (4.7 mmol) $Mo(CO)_4C_7H_8$ in 60 ml THF was warmed up to 70°C in a dry nitrogen atmosphere. After the solid was dissolved a white solid precipitated. The reaction mixture was kept at 70°C for additional 4 h. The product was filtered off and recrystallized from CH_2Cl_2 to produce white crystals of **11** in 73% (1.5 g) yield. Anal. Calcd. for $C_{20}H_{24}Mo_2N_8O_{12}P_4$: C, 27.12; H, 2.72; N, 12.67; P, 14.01. Found: C, 27.4; H, 2.9; N, 12.8; P, 14.0. IR data (Nujol): 2030 s, 1960 s, 1940 s, 1910 s, 1705 sh, 1685 s, 1410 w, 1360 w, 1320 s, 1260 w, 1220 w, 1165 w, 1015 w, 950 m, 810 m, 750 w, 710 w, 630 cm^{-1} w.

Bis(rhodiumcarbonylchloride)-bis(μ-2,4,6,8-tetramethyl-2,4,6,8-tetraaza-1λ^4-5λ^4-diphospha-bicyclo[3.3.0] octan-3,7-dione) 12. A suspension of 1.2 g (5.13 mmol) **5** and 1 g (2.57 mmol) $[Rh(CO)_2Cl]_2$ in 50 ml toluene was heated to 70°C until the evolution of CO gas ceased. After filtration and washing with CH_2Cl_2 **12** was obtained in 59% (1.2 g) yield. Anal. Calcd. for $C_{14}H_{24}Cl_2N_8O_6P_4Rh_2$: C, 21.0; H, 3.0; N, 13.99; P, 15.47. Found: C, 20.9; H, 3.2, N, 13.8; P, 15.4. IR data (Nujol): 2020 s, 1700 s, 1430 s, 1405 s, 1310 s, 1260 m, 1220 m, 1170 w, 1020 w, 965 s, 820 s, 750 s, 725 s, 630 w, 610 cm^{-1} s.

Data Collection for 6 and 10. Measurements were carried out on a Syntex $P2_1$ diffractometer, for **6** with graphite-monochromated MoK_α radiation and for **10** with graphite-monochromated CuK_α radiation. Details of the intensity data collection and the structure refinement are presented in *Table 1*. Unit cell constants were obtained by least-squares refinement of 2θ-settings for 15 high-angle reflections ± (hkl). Intensity data were collected in the θ–2θ mode to a maximum 2θ value of 50° for **6** and 105° for **10**.

TABLE 1

Experimental Details of the X-ray Diffraction Studies of **6** and **10**

	$C_{11}H_{12}N_4O_7P_2Cr$(**6**)	$C_{20}H_{24}N_8O_{12}P_4Cr_2$(**10**)
	Crystal data	
fw	426.2	796.4
space group	*P*2$_1$/*c*	*Pnma*
Unit cell constants (20 ± 1°C)		
a, Å	13.003(3)	11.270(1)
b, Å	9.924(2)	19.497(3)
c, Å	14.577(3)	14.389(4)
α, deg	90	90
β, deg	109.83(1)	90
γ, deg	90	90
Z	4	4
D_{calcd}, gcm^{-3}	1.60	1.67
	Measurement of Intensity Data	
crystal size (mm)	0.30 × 0.08 × 0.35	0.04 × 0.06 × 0.48
radiation	MoKα	CuKα
scan mode	θ-2θ	θ-2θ
scan speed, deg min^{-1}	2.02 – 9.77	2.02 – 9.77
2θ angular range	$3° \leqslant 2\theta \leqslant 50°$	$3.5° \leqslant 2\theta \leqslant 105°$
reflections measured	3096	1699
abs correction, cm^{-1}	8.0	80.5
	Structure Refinement	
I observation criterion	$I \geqslant 2.0\ \sigma(I)$	$I \geqslant 2.0\ \sigma(I)$
no. of reflections	1615	717
g (weighting factor)	0.003	0.002
R	0.078	0.108
R_w	0.066	0.091

Three control reflections were monitored every 50 reflections. No significant deviations in their intensities were observed. The net intensities of each reflection were given by $I = [P - (B1 + B2)]S$, where P is the total scan count. B1 and B2 are the stationary left and right background counts, respectively, each measured for half of the total scan time, and S is the scan rate. The standard deviation of the net intensity is then defined as

$$\sigma(I) = [P + (B1 + B2)]^{1/2}S$$

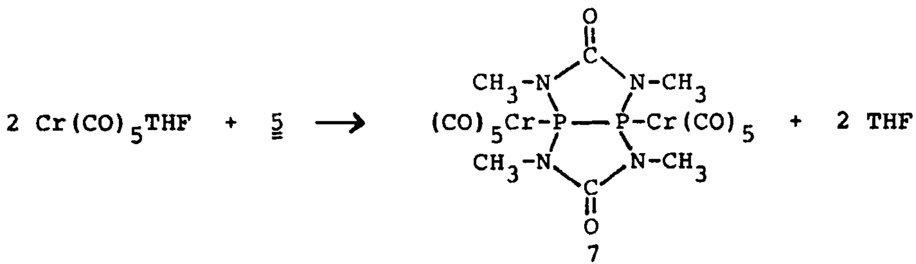
Reflections were scanned from 1.1° below the K_{α_1} to 1.1° above the K_{α_2} 2θ value. Absorption corrections were applied empirically on the basis of azimuthal scan data with ψ intervals of 20° for 20 strong reflections in various regions of reciprocal space. After reflections with $I < 2.0\ \sigma\ (I)$ had been treated as unobserved, data reduction yielded 1615 and 717 independent reflections for **6** and **10** respectively. The number of observable reflections (and hence the quality of the X-ray analysis) for both compounds, and in particular **10**, was limited by the small size of the best available crystal. In order to increase the number of observable reflections CuK_{α} radiation was employed for the intensity data collection for **10**.

Structure Solution and Refinement for 6 and 10. Both structures were solved by use of Patterson and difference syntheses. Refinement was by full-matrix least squares with $\Sigma w\Delta^2$ being minimized. Anisotropic temperature factors were introduced for all non-hydrogen atoms in **6**. The Cr atoms and two of their respective carbonyl ligands lie on a crystallographic mirror plane. Anisotropic temperature factors were introduced for all non-hydrogen atoms in **10** with the exception of the C and O atoms of the carbonyl groups which lie on the mirror plane. The methyl groups of both **6** and **10** were refined rigidly with d(C—H) = 1.08Å and tetrahedral bond angles. Group isotropic temperature factors were introduced for the hydrogen atoms. Weighing schemes were given by $w = k\ (\sigma^2(F_o) + g\ F_o^2)^{-1}$, where g was fixed at respectively 0.0003 and 0.0002. Refinement of the structures employing all measured reflections led to values of R_w of 0.094 for **6** (3096 reflections) and 0.149 for **10** (1699 reflections). The scattering factors for the non-hydrogen atoms were taken from Cromer *et al.*[4] and for the hydrogen atoms from Stewart *et al.*[5] Computations were performed on a PDP10 computer with the use of SHELX (G. M. Sheldrick), ORTEP[7] (C. K. Johnson) and locally developed programs. Atom coordinates and thermal parameters for **6** and **10** are presented in *Tables 2, 3 and 4* and tabulations of observed and calculated structure factors are available.

RESULTS AND DISCUSSION

Synthesis

The reaction of $Cr(CO)_5THF$ with the title compound, a bicyclic diphosphine, results exclusively in the formation of the 1:1 **6** and 2:1 **7** metal diphosphine complex without any oxidative cleavage of the phosphorus–phosphorus bond.



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The proposed structure[3] of **6** was confirmed by X-ray analysis. Bond distances and angles of **6** are given in Table 4.

The bischromiumpentacarbonyl complex **7** can be transferred into the gas phase without any noticeable decomposition. In the mass spectrum the molecular ion is observed at m/e 618 with 8% relative intensity. **7** can be stored in air without decomposition, it is soluble in CH_2Cl_2 and ether and can be recrystallized from THF. The ^{31}P-n.m.r. signal lies in the characteristic region for tetracoordinated phosphorus (Table 5).

TABLE 2

Atom Coordinates and Thermal Parameters (Å × 10^3) for **6** with Standard Deviations in Parentheses

atom	x/a	y/b	z/c	U_{11}[a]	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cr	0.4160(1)	0.6614(2)	0.6497(1)	43(1)	41(1)	39(1)	−7(1)	3(1)	4(1)
P(1)	0.2596(2)	0.5773(2)	0.5325(2)	36(1)	29(1)	30(1)	−3(1)	7(1)	1(1)
P(2)	0.2567(2)	0.3957(3)	0.4430(2)	47(2)	38(2)	41(2)	−8(1)	12(1)	−5(1)
N(1)	0.1627(6)	0.5101(8)	0.5730(5)	39(5)	53(6)	36(5)	0(4)	17(4)	−2(4)
N(3)	0.1757(6)	0.3132(8)	0.4941(5)	47(5)	29(5)	47(5)	−6(4)	0(4)	1(4)
N(4)	0.1930(6)	0.6713(8)	0.4329(5)	41(5)	38(5)	30(4)	−1(4)	3(3)	−1(4)
N(6)	0.1717(6)	0.4739(8)	0.3434(5)	47(5)	50(5)	26(4)	−11(4)	8(4)	−17(4)
C(1)	0.1185(9)	0.5872(12)	0.6379(7)	63(8)	84(9)	39(6)	6(6)	17(6)	19(7)
C(2)	0.1266(8)	0.3785(10)	0.5522(7)	28(6)	45(7)	46(6)	14(5)	8(5)	−6(5)
O(2)	0.0657(6)	0.3249(8)	0.5852(5)	57(5)	79(6)	63(5)	25(5)	19(4)	−15(5)
C(3)	0.1532(11)	0.1672(11)	0.4748(9)	113(11)	32(7)	87(9)	−1(7)	21(8)	−7(8)
C(4)	0.1742(9)	0.8150(9)	0.4390(7)	73(8)	43(7)	45(6)	−3(6)	3(6)	12(6)
C(5)	0.1463(8)	0.6101(9)	0.3420(7)	43(6)	40(6)	39(6)	8(5)	13(5)	−11(5)
O(5)	0.0920(5)	0.6695(7)	0.2698(4)	56(5)	71(5)	30(4)	12(4)	6(3)	−6(4)
C(6)	0.1301(9)	0.3974(11)	0.2516(7)	71(8)	67(8)	41(6)	−15(6)	5(6)	−29(7)
C(11)	0.5458(10)	0.7147(10)	0.7486(9)	57(8)	40(7)	74(8)	−13(6)	21(7)	4(6)
O(11)	0.6255(7)	0.7427(9)	0.8053(6)	57(6)	85(6)	82(6)	−33(5)	−24(5)	−6(5)
C(12)	0.4518(9)	0.7692(11)	0.5542(8)	59(8)	44(7)	49(7)	−12(6)	−3(6)	−10(6)
O(12)	0.4727(7)	0.8365(8)	0.5031(6)	101(7)	68(6)	79(6)	19(5)	35(5)	−14(6)
C(13)	0.3804(9)	0.5619(11)	0.7462(8)	57(8)	59(8)	39(6)	−7(6)	8(6)	19(6)
O(13)	0.3622(7)	0.5094(9)	0.8063(6)	97(7)	115(8)	55(5)	22(5)	41(5)	18(6)
C(14)	0.3427(9)	0.8158(12)	0.6750(7)	55(8)	57(8)	43(6)	−11(6)	1(6)	−3(6)
O(14)	0.3015(7)	0.9095(8)	0.6885(6)	78(6)	62(6)	103(7)	−37(5)	4(5)	32(5)
C(15)	0.4945(8)	0.5145(10)	0.6216(6)	32(6)	46(6)	29(5)	8(5)	0(5)	−5(5)
O(15)	0.5430(6)	0.4289(7)	0.6061(5)	53(5)	55(5)	59(5)	−1(4)	18(4)	24(4)

[a] The form of the anisotropic temperature factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}lhc^*a^* + 2U_{12}hka^*b^*)]$.

TABLE 3

Atom Coordinates and Thermal Parameters ($Å^2 \times 10^3$) for **10** with Standard Deviations in Parentheses

atom	x/a	y/b	z/c	U_{11}[a]	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cr(1)	0.0932(6)	0.2500	1.0556(5)	23(3)	107(7)	65(5)	0	−2(4)	0
Cr(2)	0.4949(6)	0.2500	0.9015(5)	36(4)	88(7)	70(5)	0	0(4)	0
P(1)	0.2339(7)	0.3351(5)	1.0662(6)	35(4)	71(7)	79(6)	−7(6)	9(5)	−1(5)
P(2)	0.3881(7)	0.3394(6)	0.9704(6)	33(4)	92(8)	63(6)	−2(6)	4(4)	0(6)
N(1)	0.3223(20)	0.3543(15)	1.1606(17)	31(14)	88(24)	62(18)	−21(18)	−14(13)	24(18)
C(1)	0.2790(29)	0.3546(18)	1.2548(21)	71(23)	81(29)	51(20)	14(23)	−3(19)	−14(23)
C(2)	0.4315(24)	0.3871(17)	1.1354(21)	33(17)	78(27)	35(19)	−28(19)	−31(17)	−7(19)
O(2)	0.4848(19)	0.4112(14)	1.2035(14)	56(14)	130(24)	60(15)	−12(16)	6(13)	−3(16)
N(3)	0.4629(25)	0.3848(15)	1.0494(16)	97(23)	94(25)	27(16)	−8(18)	5(15)	33(20)
C(3)	0.5863(29)	0.4193(21)	1.0318(25)	62(24)	124(35)	68(29)	−7(24)	29(22)	−51(25)
N(4)	0.3267(23)	0.3976(13)	0.9007(18)	69(17)	48(18)	58(18)	−3(17)	−10(16)	−27(16)
C(4)	0.3680(30)	0.4209(19)	0.8080(20)	73(24)	68(27)	53(22)	30(20)	17(20)	−15(21)
C(5)	0.2249(26)	0.4411(20)	0.9420(22)	35(20)	61(28)	57(22)	16(22)	7(17)	−9(21)
O(5)	0.1969(20)	0.4910(13)	0.9047(19)	65(14)	56(18)	124(23)	36(18)	−2(16)	−4(15)
N(6)	0.1958(19)	0.4146(11)	1.0251(16)	33(12)	37(15)	79(17)	0(15)	4(12)	−33(13)
C(6)	0.1045(30)	0.4539(17)	1.0888(23)	67(23)	80(25)	93(27)	14(24)	4(22)	25(24)
C(11)	−0.0279(24)	0.1818(20)	1.0316(21)	19(15)	126(36)	58(21)	−6(22)	20(16)	4(20)
O(11)	−0.1026(24)	0.1476(15)	1.0089(19)	57(16)	134(25)	157(25)	−12(21)	−29(17)	16(19)
C(21)	0.5956(33)	0.3137(16)	0.8442(27)	85(26)	34(21)	112(30)	−17(22)	−2(24)	−14(22)
O(21)	0.6542(25)	0.3562(16)	0.8141(21)	105(22)	118(25)	151(27)	26(22)	−6(19)	−25(20)
C(12)	0.1166(44)	0.2500	0.9307(37)	80(15)[b]					
O(12)	0.1296(32)	0.2500	0.8496(28)	104(12)					
C(13)	0.0568(37)	0.2500	1.1834(31)	59(13)					
O(13)	0.0221(28)	0.2500	1.2594(24)	85(10)					
C(22)	0.4012(45)	0.2500	0.7948(35)	80(15)					
O(22)	0.3498(29)	0.2500	0.7231(25)	94(11)					
C(23)	0.5985(45)	0.2500	1.0001(32)	73(14)					
O(23)	0.6554(27)	0.2500	1.0678(21)	70(9)					

[a] The form of the anisotropic temperature factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}K^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}lhc^*a^* + 2U_{12}hka^*b^*)]$.

[b] Isotropic temperature factors were employed for the atoms C(12)–O(23).

TABLE 4

Bond Distances (Å) and Angles (deg.) of **6**

P(1)—Cr	2.323(3)	C(11)—Cr	1.885(10)
C(12)—Cr	1.934(12)	C(13)—Cr	1.900(12)
C(14)—Cr	1.906(12)	C(15)—Cr	1.902(11)
P(1)—P(2)	2.217(4)	P(1)—N(1)	1.699(9)
P(1)—N(4)	1.695(7)	P(2)—N(3)	1.694(9)
P(2)—N(6)	1.686(7)	C(1)—N(1)	1.477(15)
C(2)—N(1)	1.386(13)	C(2)—N(3)	1.383(14)
C(3)—N(3)	1.486(13)	C(4)—N(4)	1.455(12)
C(5)—N(4)	1.396(11)	C(5)—N(6)	1.390(12)
C(6)—N(6)	1.473(12)	O(2)—C(2)	1.183(14)
O(5)—C(5)	1.203(10)	O(11)—C(11)	1.119(13)
O(12)—C(12)	1.101(15)	O(13)—C(13)	1.111(15)
O(14)—C(14)	1.124(15)	O(15)—C(15)	1.126(13)
C(11)—Cr—P(1)	175.2(3)	C(12)—Cr—P(1)	91.9(3)
C(12)—Cr—C(11)	91.4(5)	C(13)—Cr—P(1)	89.2(3)
C(13)—Cr—C(11)	87.7(5)	C(13)—Cr—C(12)	177.7(5)
C(14)—Cr—P(1)	93.5(3)	C(14)—Cr—C(11)	90.2(5)
C(14)—Cr—C(12)	87.3(5)	C(14)—Cr—C(13)	90.6(5)
C(15)—Cr—P(1)	88.0(3)	C(15)—Cr—C(11)	88.5(4)
C(15)—Cr—C(12)	89.5(5)	C(15)—Cr—C(13)	92.6(5)
C(15)—Cr—C(14)	176.5(5)	P(2)—P(1)—Cr	124.1(1)
N(1)—P(1)—Cr	116.9(2)	N(1)—P(1)—P(2)	91.1(3)
N(4)—P(1)—Cr	119.8(3)	N(4)—P(1)—P(2)	92.4(3)
N(4)—P(1)—N(1)	106.9(4)	N(3)—P(2)—P(1)	91.4(3)
N(6)—P(2)—P(1)	90.5(3)	N(6)—P(2)—N(3)	106.1(4)
C(1)—N(1)—P(1)	121.0(7)	C(2)—N(1)—P(1)	122.0(7)
C(2)—N(1)—C(1)	116.9(9)	C(2)—N(3)—P(2)	121.9(7)
C(3)—N(3)—P(2)	120.1(8)	C(2)—N(3)—C(2)	118.1(10)
C(4)—N(4)—P(1)	122.3(5)	C(5)—N(4)—P(1)	120.3(6)
C(5)—N(4)—C(4)	117.1(7)	C(5)—N(6)—P(2)	122.9(5)
C(6)—N(6)—P(2)	118.5(6)	C(6)—N(6)—C(5)	118.4(7)
N(3)—C(2)—N(1)	112.5(9)	O(2)—C(2)—N(1)	123.9(10)
O(2)—C(2)—N(3)	123.4(9)	N(6)—C(5)—N(4)	112.6(7)
O(5)—C(5)—N(4)	123.7(9)	O(5)—C(5)—N(6)	123.8(8)
O(11)—C(11)—Cr	176.7(12)	O(12)—C(12)—Cr	176.1(10)
O(13)—C(13)—Cr	176.0(9)	O(14)—C(14)—Cr	177.7(11)
O(15)—C(15)—Cr	178.5(8)		

The Lewis acids $SnCl_4$ and $SbCl_5$ form 1:1 and 2:1 adducts with **5**. On the basis of i.r. spectroscopy we assume that the tin compound **8** forms molecules in which the oxygen atoms of the carbonyl groups are coordinated to the tin. The strong absorptions at 1525 and 1515 support a cis coordination while the medium strong band at 1560 cm^{-1} can be assigned to a trans coordination. As a result of the insolubility of **8** in proton free solvents, we were not able to separate both isomers. Due to the strong absorptions at 1715 cm^{-1} of the antimonypentachloride adduct **9** we favor a coordination of the antimony via the phosphorus atoms.

We have found that **5** and $Cr(CO)_4C_7H_8$, $Mo(CO)_4C_7H_8$ and $[Rh(CO)_2Cl]_2$ in equimolar stoichiometry react to produce compounds containing a six-membered ring. The formation of three-membered rings of type **10a** was not observed.

10 forms colorless crystals which were purified by recrystallization from CH_2Cl_2. The ^{31}P-n.m.r. spectrum allows no definite statement of the symmetry and bonding of the phosphorus ligand since only one sharp singlet has been observed at

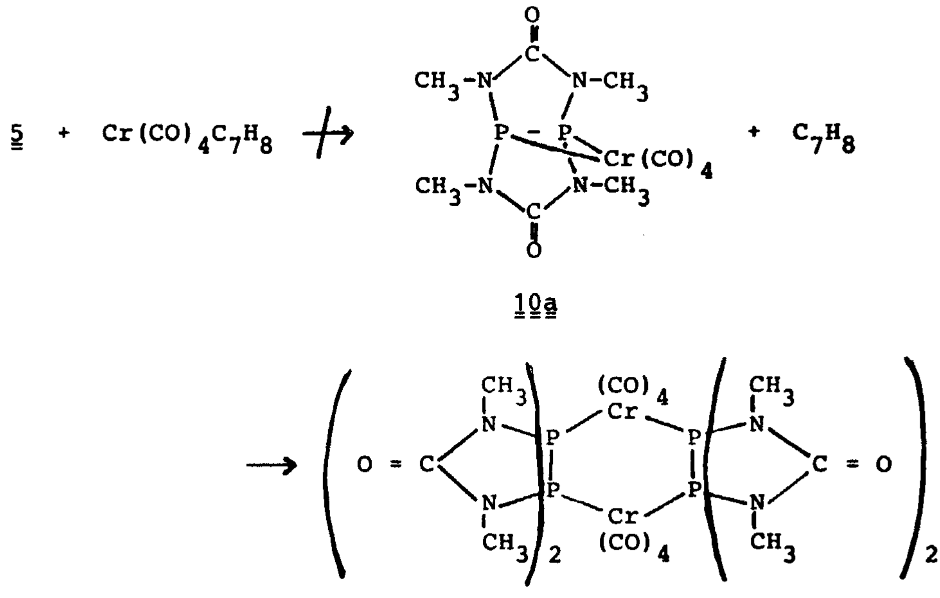
TABLE 5

Summary of n.m.r. data for **7**, **10**, **11** and **12**

Compound		Chemical Shifts (ppm)[a]		Coupling Constants (Hz)
		^{1}H	^{31}P	
$P_2[meNC(O)Nme\ Cr(CO)_5]_2$	**(7)**	3.2	119.9	J_{PNCH}, 4.5
$P_4[meNC(O)Nme]_4[Cr(CO)_4]_2$	**(10)**	3.25	55	J_{PNCH}, 4.5
$P_4[meNC(O)Nme]_4[Mo(CO)_4]_2$	**(11)**	3.2	71.1	J_{PNCH}, 4.5
$P_4[meNC(O)Nme]_4[Rh(CO)Cl]_2$	**(12)**	3.25	57,52	$J_{P\text{-}P}$, 186.1

[a] See Experimental Section for statement of references used. All substances were dissolved in CH_2Cl_2.

$\delta = +55.0$ ppm. In comparison the 1:2 $Cr(CO)_5$ complex **7** exhibits one resonance signal at $\delta = +119.9$ ppm. The n.m.r. data are summarized in Table 5. In methylenchloride the osmometric molecular mass determination was found to be 877. The value lies in the range of the dimer **10**. The mass spectrum of **10** shows as the highest fragment the diphosphine of **5** at m/e = 234. An unambiguously structural assignment could only be made by an X-ray structural analysis. The reaction of **5** with the corresponding molybdenum complex results in the formation of **11**. In analogy to **10**, a six-membered ring with two metal and four phosphorus atoms is assumed for **11** and the rhodium chloride complex **12**.



10a

10

Discussion of the Molecular Structures of 6 *and* 10

Perspective views of the molecular structures of **6** and **10** are given in Figures 1 and 2. A dimeric structure for **10** is confirmed by the X-ray structural analysis. Only minimal distortion of the octahedral coordination geometry of the Cr-atom in **6** is observed. The Cr—P(1) distance of 2.323(3) Å lies in the middle of the region of known Cr—P bond lengths, which range from 2.25 Å in *trans*-$Cr(CO)_4[P(OC_6H_5)_3]_2$[8]

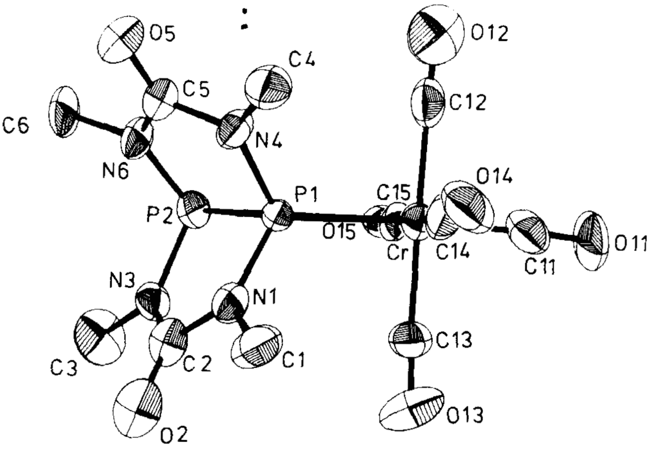


FIGURE 1 Structure of **6** with atomic numbering.

to 2.42 Å in [(triphos)CO(δP_3)$Cr_2(CO)_{10}$].[9] An indication of a trans-effect in **6** is given by the fact that the Cr—C(11) bond distance of 1.885(10) Å is shorter than those of the other Cr—C bonds. This difference is not, however, significant. In contrast, a pronounced shortening of the Cr—C bond *trans* to the Cr—P bond of 0.043 and 0.061 Å relative to the mean values of the other Cr—C bond pairs has been observed in the analogous complex $P_4(SiMe_2)_3Cr(CO)_5$.[10] The bicyclic phosphine ligand in **6** displays an "open-book" arrangement of the two five-membered P_2N_2C rings joined along the P—P bond. The λ^3P—λ^4P distance of 2.217(4) Å is similar to that of 2.222(2) Å observed for the λ^3P—λ^3P bond in the free ligand.[3] These values fall within the typical range (2.16–2.24 Å) for the P—P bond length, which is independent of oxidation state and nature of the substituents.[11] The molecular dimen-

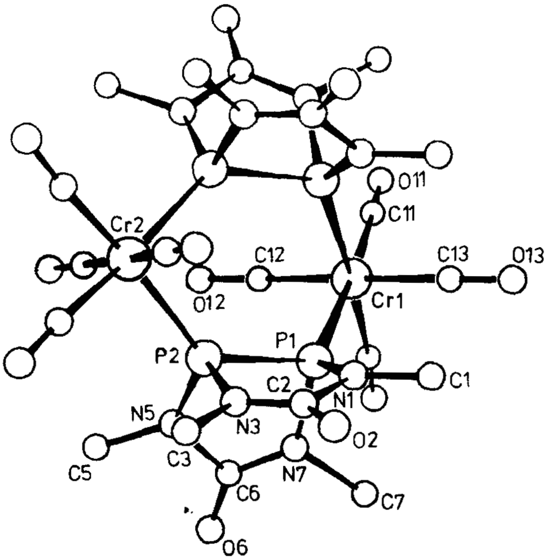


FIGURE 2 Structure of **10** with atomic numbering.

sions of the bicyclic ligand in **6** are in accordance with an approximate C_{2v}-symmetry.

The very limited quality of the X-ray analysis of **10**, which is a consequence of the small size of the best available crystal, precludes a detailed discussion of bond lengths and angles.

10 displays crystallographic C_h-symmetry with both Cr-atoms and two of their respective CO-ligands lying in the mirror plane. The Cr—P distances of 2.30(1) and 2.34(1) Å are similar to that in **6**. The bicyclic phosphine ligands display the "open-book" arrangement. The λ^4P-λ^4P distance of 2.22(1) Å is similar to the λ^3P-λ^4P distance in **6** and the λ^3P-λ^3P distance in the free ligand, thereby underlining the independence of the P—P bond length from the oxidation state of the P atoms. A similar dimeric structure has been found for $[P_4(Sime_2)_3Cr(CO)_4]_2$.[10]

Supplementary Material Available:

Compilations of observed and calculated structure factors on an absolute scale (pages). Ordering information is given on any current masthead page.

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